2872 *Macromolecules* **1999,** *32,* 2872−2875

Emulsion Polymerization of *n*-Butyl Methacrylate by Reverse Atom Transfer Radical Polymerization

Jian Qiu, Scott G. Gaynor, and Krzysztof Matyjaszewski*

Center for Macromolecular Engineering, Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213

Received October 29, 1998; Revised Manuscript Received February 17, 1999

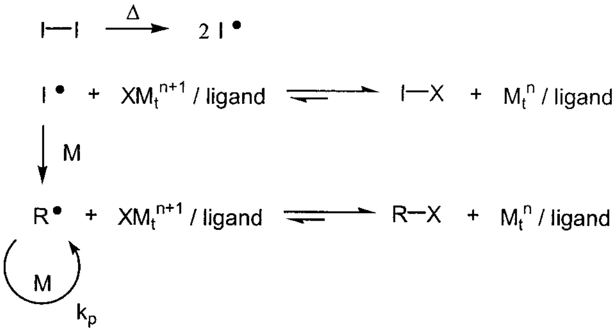
ABSTRACT: The controlled/“living” radical polymerization of *n*-butyl methacrylate was conducted in an emulsion under reverse atom transfer radical polymerization (ATRP) conditions. The initiators used were conventional water-soluble initiators, such as potassium persulfate (KPS), 2,2′-azobis(2-methylpropionamidine) dihydrochloride (V-50), and 2,2′-azobis[2-(2-dimidazolin-2-yl)propane] dihydrochloride (VA-044). The transition metal catalyst employed was copper(II) dibromide with 4,4′-dialkyl-2,2′-bipyridine as the ligands.

Emulsion polymerization has been a successful industrial process since the mid-1930s. The major advantages of this technique include the use of an environmentally friendly solvent (water), efficient heat transfer, less viscous reaction media, fast polymerization rates, and high monomer consumption.[1−3] Although this process has been widely used, and many methods to control the properties of the emulsion polymers are available, there is at least one problem to be solved: how to produce polymers with well-defined molecular weights and narrow molecular weight distributions in emulsion?

A potential solution to this problem might be the controlled/“living” radical polymerization methodology.[4] Among many existing approaches, the most prosperous ones are the nitroxide-mediated polymerization,[5−9] atom transfer radical polymerization (ATRP),[10−14] degenerative transfer,[15] and reversible addition-fragmentation chain transfer (RAFT).[16] However, when these techniques, successful in bulk or solution polymerization, are applied to emulsion polymerization, the heterogeneous nature of the system may complicate the kinetics of the exchange between the active and dormant radicals, a key factor in obtaining a controlled/“living” polymerization. To maintain the “living” character of the polymerization in a stable emulsion, many issues need to be considered, for instance, the choice of an appropriate surfactant, the solubility of the initiator and the radical trapping agent in both the organic and aqueous phases, avoidance of any potential side reactions caused by water, reaction temperature, etc. For nitroxide-mediated polymerizations, both seeded[17] and ab initio[18] emulsion polymerizations of styrene have been reported. Unfortunately, due to the low homolytic dissociation constants of the alkoxyamines, high temperatures (>125 °C) and pressures have to be employed to achieve a reasonable polymerization rate for the emulsions. The RAFT process has also been applied to emulsion polymerization.[16] Nevertheless, the stability of the emulsion and the particle size were not addressed.

Recently, we reported our work on extending ATRP to water-borne systems.[19] Well-defined polymers were obtained for *n*-butyl methacrylate, *n*-butyl acrylate, methyl methacrylate, and styrene, as evidenced by low polydispersities (<1.4) and molecular weights close to predicted values ($DP_n = \Delta[M]/[I]_0$). The resulting latexes were visually stable from days to weeks. However, due to the use of an organic soluble initiator, the mechanisms of nucleation and particle growth are unclear and may be susceptible to the sequence of initiator addition. To be assured that radicals can be generated in the aqueous phase and that the resulting polymerization is controlled, reverse atom transfer radical polymerization was explored.

Scheme 1



Starting from a conventional radical initiator and a high-valent transition metal complex, reverse ATRP approaches the equilibrium between dormant species and free radicals through the mechanism illustrated in Scheme 1. Upon decomposition of the initiator (I−I) into radicals, these radicals then can initiate the polymerization of monomer and then react with the deactivator (XM_t^{n+1}). The initial radicals can also react directly with the deactivator as well. The net result is that the halide initiator and the lower oxidation state, transition metal catalyst are generated in situ. Because we were using ligands that contained long alkyl groups (vide infra), it was expected that the catalyst would be confined to the monomer (polymer) droplets (particles) or in micelles. The initiation would occur as in a conventional emulsion; the initiator radicals would add monomer that was dissolved in the aqueous phase (homogeneous nucleation) or in the micelles (micellar nucleation).

Both copper-[12,20] and iron[21]-based reverse ATRP, in bulk or in solution, have been reported. The desire to extend this method to emulsion is obvious: many water-soluble initiators in conventional emulsion polymerization have been well studied, and the nucleation mechanism is therefore less questionable. A previous investigation employing a similar approach was carried out

10.1021/ma981695f CCC: $18.00

Table 1. Emulsion Polymerization by Reverse ATRP Using KPS as the Initiator[a]

entry	T (°C)	buffer	time (h)	conversion (%)	$M_{n,sec}$	M_w/M_n	initiation efficiency [f]
1	90	none	20	no polymer			
2	70	none	26	no polymer			
3	90	$NaHCO_3$[b]	3.3	88	119 400	1.55	0.2
4	90	KH_2PO_4/NaOH[c]	3.2	85	106 100	1.71	0.2
5	70	KH_2PO_4/NaOH[c]	5	72	53 100	1.36	0.4
6[d]	70	KH_2PO_4/NaOH[c]	4	44	20 700	1.10	0.3
7[e]	70	KH_2PO_4/NaOH[c]	2	25	20 800	1.22	0.4
			4.4	46	33 630	1.19	
			7.8	61	43 640	1.22	
			20.3	92	52 180	1.25	

[a] All the polymerizations are conducted under the following conditions, unless noted: $[KPS]_0/[BMA]_0 = 1/400$; $[KPS]_0/[CuBr_2]_0/[dAbpy]_0 = 1/1.5/3$; $[BMA]_0/[water] = 1.5/10$ (v/v); Brij 98: 2 wt % vs water. [b] The concentration of $NaHCO_3$ in aqueous phase: 0.57 mg/mL. [c] A commercially available buffer solution (pH = 7) was used in place of deionized water. [d] $[KPS]_0/[BMA]_0 = 1/200$. [e] $[KPS]_0/[CuBr_2]_0/[dAbpy]_0 = 1/2/4$. [f] The initiation efficiency was calculated as $M_{n,th}/M_{n,sec}$, $M_{n,th} = M_0 \times \Delta[M]/[I]_0$.

Table 2. Emulsion Polymerization by Reverse ATRP Using Azo-Compounds as the Initiator[a]

entry	initiator	T (°C)	$CuBr_2$[b]	time	conversion (%)	$M_{n,sec}$	M_w/M_n	initiation efficiency
1	V-50	90	none	5 min	48	359 300	3.59	<0.1
				10 min	95	281 300	3.42	
				15 min	98	255 500	3.56	
2	V-50	90	1 equiv	24 min	9	17 520	1.40	0.4
				1.5 h	67	52 130	1.28	
				5 h	92	69 250	1.26	
3	V-50	90	1.5 equiv	36 min	10	10 930	1.22	0.3
				2.2 h	53	53 190	1.20	
				7 h	92	77 400	1.23	
4	V-50	90	2 equiv	1 h	18	9 890	1.24	0.2
				3 h	37	47 900	1.08	
				5.9 h	60	76 200	1.19	
5	VA-044	70	1.5 equiv	4 h	37	15 300	1.43	0.7
6	VA-044	80	1.5 equiv	3.5 h	50	26 100	1.32	0.5
				6.3 h	79	40 300	1.31	
				9 h	84	47 300	1.28	

[a] All polymerizations were conducted under the following conditions, unless noted: $[I]_0/[BMA]_0 = 1/400$; $[CuBr_2]_0/[dAbpy]_0 = 1/2$; $[BMA]_0/[water] = 1.5/10$ (v/v); Brij 98: 2 wt % vs water. [b] $[CuBr_2]_0/[I]_0$.

without complete success.[22] We believe that the failure lies in the choice of both the surfactant and the ligand. The wrong selection may lead to a lack of the deactivator in the monomer droplets/polymer particles where the polymerization takes place, resulting in either uncontrolled polymerization or very low conversion. Our earlier results showed that by using a nonionic surfactant, i.e., Brij 98, and a ligand with long alkyl chains, either 4,4′-di(5-nonyl)-2,2′-bipyridine (dNbpy) or 4,4′-dialkyl-2,2′-bipyridine (dAbpy, a mixture of 5-nonyl- and 1-pentyl substituted bpy), these problems could be overcome.[19] Similar conditions were therefore employed in reverse ATRP, using Cu(II) dibromide as the transition metal. The monomer, *n*-butyl methacrylate (BMA), was chosen mainly because of the stability of the derived alkyl halide in water and fast polymerization rate under ATRP conditions.

Potassium persulfate (KPS) was first used as the initiator. However, no polymer was observed after more than 20 h, at either 70 or 90 °C (Table 1, entries 1 and 2). It is known that during the decomposition of KPS a side product, HSO_4^-, is generated by the reaction of $S_2O_8^{2-}$ with water. The accumulation of HSO_4^- changes the pH of the medium, lowering the initiation efficiency and the polymerization rate.[23,24] Further, in an ATRP system, such acidic conditions may adversely affect the catalyst activity. Applying a buffer solution (Table 1, entries 3−7) solved the problem of lack of polymerization.

Reasonable polymerization rates were obtained at both 70 and 90 °C, although the polymerizations were not well controlled at 90 °C. This was attributed to a high degree of termination as a result of too many radicals generated at the higher temperature. By reducing the temperature to 70 °C, well-controlled polymerizations were achieved.

The latexes from the polymerizations were quite stable, except when sodium bicarbonate was used as the buffer. In this case, coagulation occurred during the polymerization. One would expect that the polymer particles should be formed in a manner consistent with a conventional emulsion, either by homogeneous or micellar nucleation, as the radicals are generated in the aqueous phase and the deactivator, $Cu(II)Br_2$/dAbpy, should be in the organic phase. However, the particle sizes of those stable latexes were larger than expected for a normal emulsion polymerization (<1 μm). For example, the sample from Table 1, entry 5, has a number-average diameter $d_n = 2.51\ \mu$m, $d_w/d_n = 2.07$. Aggregation of the particles while standing may play a role for the measured large particle size. Another possible cause for the large particle size, as well as the observed coagulation, is the buffer used. The electrolytes in the buffer solution may greatly influence the colloidal stability of the latex and the particle size. It may be possible to obtain particles of smaller size by reducing the concentration of the salts in the buffer solution or by other changes in the surfactant mixture. Such possibilities are currently under investigation.

Unlike KPS, another class of widely used water-soluble initiators, azo compounds, are seldom involved in side reactions with water. Therefore, by choosing azo initiators, a buffer solution was unnecessary, helping to simplify the system. Both of the two azo initiators

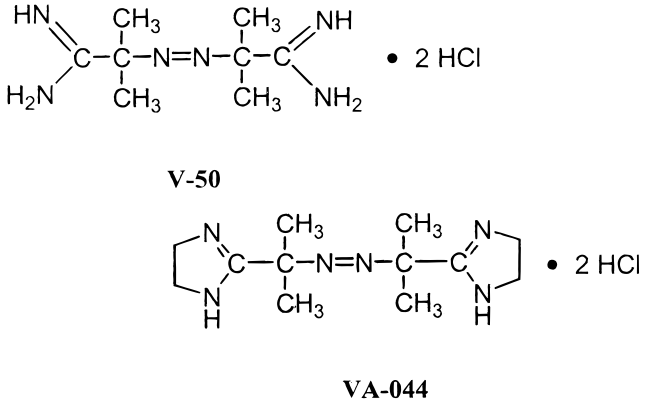


Figure 1. Chemical structures of the azo initiators.

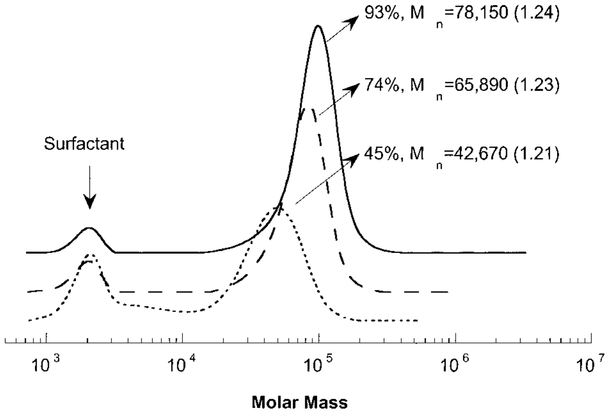


Figure 2. SEC chromatograms of the emulsion polymerization by reverse ATRP using V-50 as the initiator. $[\text{V-50}]_0/[\text{BMA}]_0 = 1/400$; $[\text{CuBr}_2]_0/[\text{dAbpy}]_0 = 1/2$; $[\text{CuBr}_2]_0/[\text{V-50}]_0 = 1.5/1$; $[\text{BMA}]_0/[\text{water}] = 1.5/10$ (v/v); Brij 98: 2 wt % vs water.

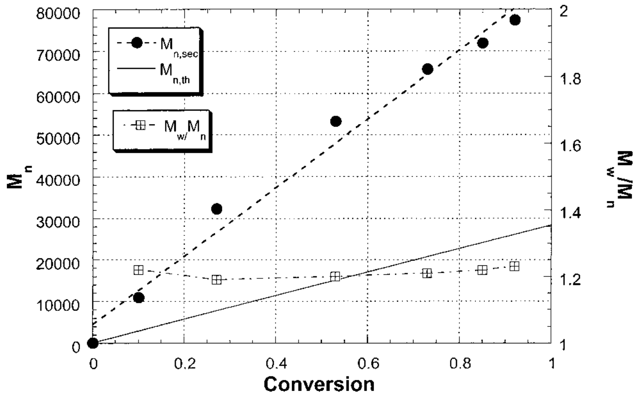


Figure 3. Dependence of molecular weight on monomer conversion for the emulsion polymerization by reverse ATRP (Table 2, entry 3).

used, 2,2′-azobis(2-methylpropionamidine) dihydrochloride (V-50) and 2,2′-azobis[2-(2-dimidazolin-2-yl)propane] dihydrochloride (VA-044, Figure 1), led to well-controlled polymerizations. Polymers of low polydispersities were obtained (Figure 2), with molecular weights increasing linearly with conversions (Figure 3).

The amount of initial CuBr_2 played an important role in the polymerization rate and the level of molecular weight control. Without CuBr_2 the emulsion polymerization was completely uncontrolled (Table 2, entry 1), as expected. As more CuBr_2/ligand was added, slower polymerization rates (Figure 4) and narrower molecular weight distributions were observed, which was consistent with the role of CuBr_2/ligand as a deactivator.

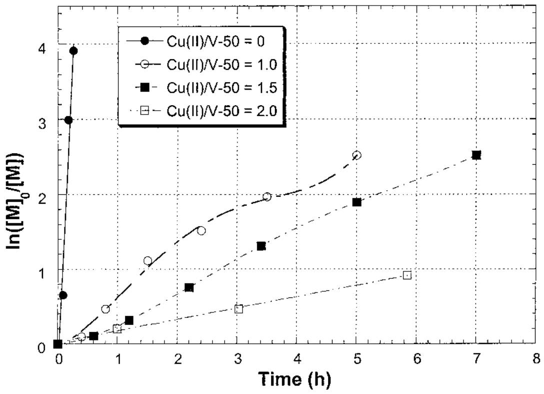


Figure 4. Kinetics of emulsion reverse ATRP under different $[\text{CuBr}_2]_0/[\text{I}]_0$ ratios (Table 2, entries 2−4). The curve fitting is only added to aid the eye.

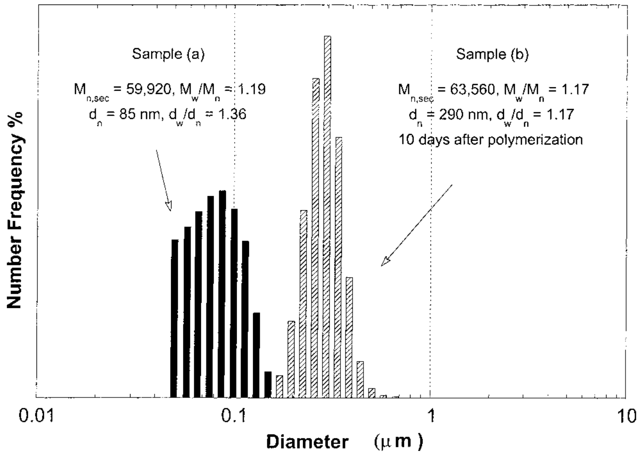


Figure 5. Particle size distributions of the latexes prepared by reverse ATRP emulsion, as measured by laser diffraction (Horiba LA-900).

However, the initiation efficiencies were low. Preliminary UV−vis and EPR studies indicated that, although dAbpy is much better than bpy in confining CuBr_2 to the organic phase, a large portion of CuBr_2 is present in the aqueous phase, uncomplexed by dAbpy. Being excellent radical scavengers, these Cu(II) salts likely terminate radicals in the aqueous phase but do not reinitiate the polymerization. Since these oligomers are water-soluble, they would remain in the aqueous phase and are not, or are very slowly, reinitiated, thus reducing the overall initiator efficiency. Because a subtle balance between the organic and aqueous solubility of the catalyst/deactivator can play such a critical role, improving the initiation efficiency may require the use of a new ligand and/or different polymerization conditions.

The particle size and particle size distribution of the latex prepared by reverse ATRP using V-50 as the initiator were measured by laser diffraction. Shown in Figure 5 are two examples. Sample a, measured right after the polymerization, has a number-average diameter of d_n= 85 nm, $d_w/d_n = 1.36$; sample b was measured after being stored at room temperature for 10 days, with $d_n = 290$ nm, $d_w/d_n = 1.17$. The relatively stable latex and small particle size (submicron) suggest a true emulsion nature of these polymerizations.

Experimental Section

n-Butyl methacrylate was distilled under vacuum after being washed with a 10% $\text{NaOH}_{(aq)}$ solution and sparged with nitrogen just prior to use. Deionized water was used without further purification. The buffer (monobasic potassium phosphate and sodium hydroxide, pH = 7.0) was obtained from Fisher and used as received. All other reagents were used as received. The dialkylbipyridines were synthesized as described previously.[25] Latexes withdrawn from the reaction flask were dissolved in THF and directly injected to a Shimadzu GC-14 gas chromatograph. From the residual monomer content in the samples, conversions were obtained. After the GC samples were dried over $MgSO_4$ and the copper complex removed by passing through an alumina column, molecular weights were determined by injecting the solution onto the SEC columns (Polymer Standard Service 10^5, 10^3, and 100 Å and guard). A calibration curve based on linear poly(methyl methacrylate) standards was used in conjunction with a differential refractometer. The particle sizes of the resulting colloids were determined by laser diffraction using a Horiba LA-900 instrument.

General Polymerization Example. To a 25 mL Schlenk flask were added $CuBr_2$ (8.0 mg), dAbpy (27.3 mg), hexadecane (0.15 mL, as GC standard), Brij 98 (0.2 g), and a magnetic stir bar; the flask was then sealed and deoxygenated by applying vacuum and backfilling with nitrogen. Previously degassed *n*-BMA (1.5 mL) was then added. The mixture was stirred at 90 °C until a homogeneous solution was obtained (~20 min). After the flask was cooled to room temperature, 5 mL of degassed water was added to form an emulsion with vigorous stirring. In a separate flask, V-50 (9.0 mg) was dissolved in 7 mL of degassed water, and 5 mL of that was transferred via syringe to the emulsion prepared above. The flask was placed in an oil bath set at 90 °C. The reaction mixture was stirred at 1100 rpm by magnetic stirring. (N.B.: the stir bar must be of sufficient size to allow for effective stirring and to obtain a stable emulsion at high monomer conversions.) Samples were taken periodically by syringe to monitor conversion (GC) and molecular weight (SEC).

Conclusions

Reverse ATRP was successfully applied to the emulsion polymerization of *n*-butyl methacrylate by using water-soluble initiators. The "living" character of the polymerization was maintained as evidenced by a linear increase of the molecular weights with conversion and narrow molecular weight distributions, albeit with relatively low initiator efficiencies, ca. 0.4. Different initiation systems required the use of different, optimized reaction conditions.

To better understand the mechanism of nucleation and particle growth in these unique systems, further detailed kinetic studies are necessary and are being conducted. The extension of this controlled/"living" emulsion polymerization to other monomers, such as *n*-butyl acrylate, styrene, methyl methacrylate, etc., as well as for the synthesis of copolymers and other materials, is the focus of current research and will be the subject of a future publication.

Acknowledgment. We are grateful to Dr. Christina Jasieczek at PPG Industries for particle size measurements. Finacial support from the industrial members of the ATRP Consortium at CMU is also greatly appreciated.

References and Notes

(1) Gilbert, R. G. *Emulsion Polymerization. A Mechanistic Approach*; Academic Press: London, 1995.
(2) *Emulsion Polymerization and Emulsion Polymers*; Lovell, P. A., El-Aasser, M. S., Eds.; John Wiley and Sons: Chichester, 1997.
(3) *Emulsion Polymerization*; Piirma, I., Ed.; Academic Press: New York, 1982.
(4) *Controlled Radical Polymerization; ACS Symposium Series*; Matyjaszewski, K., Ed.; American Chemical Society: Washington, DC, 1998; Vol. 685.
(5) Solomon, D. H.; Rizzardo, E.; Cacioli, P. US 4 581 429, 1985.
(6) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987.
(7) Hawker, C. J.; Elce, E.; Dao, J.; Volksen, W.; Russell, T. P.; Barclay, G. G. *Macromolecules* **1996**, *29*, 2686.
(8) Fukuda, T.; Terauchi, T.; Goto, A.; Ohno, K.; Tsujii, Y.; Miyamoto, T. *Macromolecules* **1996**, *29*, 6393.
(9) Greszta, D.; Matyjaszewski, K. *J. Polym. Sci., Polym. Chem.* **1997**, *35*, 1857.
(10) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721.
(11) Wang, J. S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614.
(12) Wang, J. S.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 7572.
(13) Patten, T. E.; Xia, J.; Abernathy, T.; Matyjaszewski, K. *Science* **1996**, *272*, 866.
(14) Matyjaszewski, K. *Macromolecules* **1998**, *31*, 4710.
(15) Gaynor, S. G.; Wang, J. S.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 8051.
(16) Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. G.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559.
(17) Bon, S. A. F.; Bosveld, M.; Klumperman, B.; German, A. L. *Macromolecules* **1997**, *30*, 324.
(18) Marestin, C.; Noel, C.; Guyot, A.; Claverie, J. *Macromolecules* **1998**, *31*, 4041.
(19) Gaynor, S. G.; Qiu, J.; Matyjaszewski, K. *Macromolecules* **1998**, *31*, 5951.
(20) Xia, J.; Matyjaszewski, K. *Macromolecules* **1997**, *30*, 7692.
(21) Moineau, G.; Dubois, P.; Jerome, R.; Senninger, T.; Teyssie, P. *Macromolecules* **1998**, *31*, 545.
(22) Makino, T.; Tokunaga, E.; Hogen-Esch, T. E. *Am. Chem. Soc., Polym. Prepr.* **1998**, *39* (1), 288.
(23) Behrman, E. J.; Edwards, J. O. *Rev. Inorg. Chem.* **1980**, *2*, 179.
(24) Lock, M. R.; El-Aasser, M. S.; Klein, A.; Vanderhoff, J. W. *J. Appl. Polym. Sci.* **1990**, *39*, 2129.
(25) Matyjaszewski, K.; Patten, T.; Xia, J. *J. Am. Chem. Soc.* **1997**, *119*, 674.

MA981695F